

Calculating the influence of external charges on the photoluminescence of a CdSe quantum dot

Lin-Wang Wang

NERSC, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

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Abstract

The influence of external charges on the radiative recombination rate of an electron-hole pair in a CdSe quantum dot is investigated via atomistic empirical pseudopotential calculations. It is found that, when a negative external charge is near the surface of a CdSe quantum dot, its Coulomb potential could be strong enough to pull the hole away from the electron, and results in a reduction of the radiative recombination rate by a factor of 70. Distance, direction, charge number and charge type dependences of this effect are investigated.

1 Introduction

Colloidal CdSe quantum dot is one of the most studied quantum dot systems. Its optical spectra have been studied in both experiment[1] and theory [2]. Recent experiments have shown rich phenomena related to external and surface charges of the CdSe quantum dots (QD). These include: the direct measurement of net charge on a single QD and its blinking effects [3], photoluminescence (PL) spectral shifting of a single QD [4], permanent dipole moment of a QD [5], and PL blinking (intermittency) of a single QD [6]. The recent experimental finding [7] of the correlation between the spectral shifting and PL blinking demonstrated that surface trapped charges are involved in both processes. But theoretical studies of the effects of surface localized charges on PL radiative rate and on PL energy are rare. In this paper, we present one such study using empirical pseudopotential calculations. We will focus on the charge effects on the radiative recombination rate.

CdSe quantum dots have been used as multicolor fluorescence markers for biological labeling [8]. However, photoluminescence intermittency phenomenon has limited the performance of such markers. Using single particle spectroscopy, it was found that [6] the PL from a single CdSe quantum dot can go off for a period (which could be a few seconds) (off-period), then come back on for a period (on-period). Although PL intermittency has also been found in large molecules [9], the underlying physics is probably very different.

It has been proposed that [10], the intermittency is caused by ionization of the quantum dot. Under repeated photon excitation, once for a while, two electron-hole pairs could be excited simultaneously. Then, one electron-hole pair may recombine through Auger channel, and emit one hole (or electron) outside the quantum dot. This emitted carrier will be trapped in the surrounding medium for some time. During this time (off-period), the left-behind oppositely charged delocalized carrier in the quantum dot will generate a very fast nonradiative Auger channel for any excited electron-hole pairs in the future. This delocalized carrier will remain inside the quantum dot during this off-period (due to possible different barrier heights for electron and hole). As a result, during this off-period, the radiative luminescence is quenched.

However, some aspects of this Auger quenching model have been challenged recently [11, 12]. First, according to the model, the ionization rate should be proportional to the square of the incoming light intensity. In ex-

periments [11, 12], a linear dependence is found. Thus, instead of double electron-hole pairs, the ionization might only involve a single electron-hole pair [11]. Besides, the Auger emission for the PL quenching during the off-period has yet to be proved experimentally. One needs to demonstrate whether indeed a delocalized free carrier is inside the QD during the off-period. While the typical free carrier life time needed in the Auger quenching model is about 1 second [10], recent infra-red experiments show that the delocalized electron life time is ~ 1 ns [13] (with hole life time even shorter).

Given the uncertainty about the Auger quenching model, it is helpful to study the plausibilities of alternative models. In one such model, a carrier (or two with opposite charge signs) is trapped near the surface. This trapped charge is created from the ionization process described above. After both the excited electron and hole are trapped (maybe one near the surface, one far away, or both near the surface), there will be no “untrapped” delocalized carrier inside the quantum dot, thus no Auger effect. But the trapped charge can pull apart the future excited electron from the excited hole in real space via Coulomb interaction. Due to the reduced spatial overlap, their optical recombination oscillator strength will be reduced. As a result, the PL is less competitive to the normal nonradiative channel, thus becomes weak.

One essential question of this alternative model is whether the Coulomb potential of a trapped charge near the surface is strong enough to pull apart the electron-hole pair and significantly reduces the optical matrix element. In this paper, an atomistic empirical pseudopotential calculation is used to address this question. This empirical pseudopotential method (EPM) has been used successfully to study CdSe quantum dot band gaps [14], dielectric constants [14], higher excited states [2] and exciton exchange-correlation effects [15]. The atomistic feature of this method makes it ideal to study possible localized states, which are beyond the valid regimes of continuum methods like effective mass and k.p model. At the same time, the efficiency of this method comparing to the ab initio calculations enables us to deal with thousand atom systems with ease.

2 Calculation

A CdSe wurtzite structure quantum dot is constructed by keeping the atoms inside a sphere and removing the surface atoms with only one bond connecting to the rest of the quantum dot. The dangling bonds of surface Cd and Se atoms are passivated by short range ligand potentials, so there will be no

band gap surface state. The detail of the pseudopotentials and passivations have been reported else where [14]. The calculated band gap as a function of quantum dot size agrees well with the experimental result[14]. Although most experiments on PL intermittency are carried out on CdSe/CdS core/shell structures, the calculation is done here for the CdSe passivated core alone. The situation of the core/shell structure will be discussed at the end of the article.

In an EMP calculation, the single particle wavefunction ψ_i and its eigen energy ϵ_i are solved from the Schrodinger's equation:

$$[-\frac{1}{2}\nabla^2 + V(r) + \hat{V}_{nonloc}]\psi_i = \epsilon_i\psi_i, \quad (1)$$

here, $V(r)$ is the total potential of the system. If no external charge is presented, $V(r)$ is generated nonselfconsistently as $V_{dot} = \sum_R v_\alpha(r - R)$, where $v_\alpha(r - R)$ is the atomistic empirical pseudopotential of atomic type α fitted to experimental band structure. In Eq(1), \hat{V}_{nonloc} is the nonlocal part of the pseudopotential (including the spin-orbit interactions). It is represented in a real space Kleinman-Bylander form [16]. Due to the spin-orbit interaction, ψ_i has spin up and spin down components. Each component is expanded in a planewave basis. Equation (1) is solved for a few states near the band gap using the folded spectrum method [17], via a computer code named Escan.

Since total electron charge density is not solved selfconsistently in our approach, we will use a classical model to describe the dielectric screening of an external charge (the trapped charge). Using a dielectric constant ϵ , an external point charge Z at radius s outside a sphere of radius a will produce a screened electric static potential as

$$V_{ext}(\mathbf{r}) = Z \sum_{n=0}^{\infty} \frac{2n+1}{\epsilon n + n + 1} \frac{r^n}{s^{n+1}} P_n(\cos\theta) \quad for \quad r < a, \quad (2)$$

and similar formulas for the regions of $s > r > a$ and $r > s$ as given in Ref[18]. In Eq(2), θ is the angle between \mathbf{s} and \mathbf{r} , and we have assumed vacuum outside the quantum dot. To see how much V_{ext} will change the electron and hole wavefunctions, we have add it to V_{dot} and used $V(r) = V_{ext} + V_{dot}$ in Eq(1). The wavefunctions ψ_i for electron and hole are re-solved. However, the Coulomb attraction between the excited electron and hole will move them closer together. To include this effect, we have calculated the Coulomb potential generated by the electron and hole wavefunctions ψ_i ,

$$V_{coul}(r) = \int \frac{|\psi_i(r')|^2}{\epsilon|r-r'|} d^3r' . \quad (3)$$

This Coulomb potential V_{coul} of electron (hole) is used to give $V(r) = V_{dot} + V_{ext} \pm V_{coul}$ in Eq(1) to re-solve new hole (electron) wavefunctions. This selfconsistent iteration can be repeated until its convergence. In reality, we found that one iteration is good enough to give 95% of the correction. Since we are interested in the PL quenching, the optical transition matrix-element-square (P) is the most important property we will look at. This is calculated between the conduction band minimum (CBM) and valence band maximum (VBM) as $P = \sum_{j=x,y,z} |\langle \psi_{cbm} | \nabla_j | \psi_{vbm} \rangle|^2$. Notice that, we will ignore any atomic relaxations due to the excited electron-hole pair. Thus, this P (matrix-element-square) is the same for absorption (of this peak) and emission. P is inversely proportional to the radiative life time.

We will concentrate on one CdSe quantum dot, which has 534 Cd atoms and 527 Se atoms, corresponding to a diameter of 39 Å. To describe the geometry of the quantum dot, let's first align the wurtzite c axis with the Cartesian z direction. Then, the quantum dot is consisted with alternating Se and Cd layers in x-y plane. The positive z direction is the direction from Cd to Se atom where they form a z-direction bond. The top (positive z) of the QD is terminated by a small Cd layer, with one Cd atom at the center. The bottom of the QD is terminated by a small Se layer, with three Se atoms surrounding the center (but no one Se atom is at the center). The radius a used in Eq(2) will place the top of the sphere 0.5Å above the top Cd layer and the bottom of the sphere 0.5Å below the bottom Se layer.

3 Results and discussion

We first place a negative charge (a trapped electron) on top of the quantum dot. We will specify the position of this external charge by its distance d to the top center Cd atom of the dot. We have calculated the cases of $d = 0.5, 1.5, 2.5, 4.5$ Å. The closest distance of 0.5 Å is used to represent a dangling bond trapped charge position. Notice that, although Cd atoms are usually passivated by the TOPO molecules, for the unpassivated Cd dangling bonds, they are the trapping sites for electrons [19]. The results for eigen energies, P , and the centers of mass positions of electron and hole wavefunctions (before and after the Coulomb interaction selfconsistency) are listed in Table I. The charge density plots of the electron and hole wave-

functions for $d = 0.5\text{\AA}$ is shown in Fig.1. From the numerical results, we have the following observations:

(1) When there is no external charge, the electron and hole wavefunctions are located near the center of the quantum dot. (The zero of z is defined at one central Se atom layer. Since there is no inversion symmetry, the electron and hole wavefunctions need not to be located at exactly $z=0$). The Coulomb selfconsistency barely changes the P at all. But the band gap is reduced by the Coulomb energy by about 140meV. The optical transition P equals $0.127(a.u)(\equiv P_0)$, corresponding to a radiative life time of about 2 ns (this does not include the exchange interaction between electron and hole, which creates a nonradiative ground state of the exciton, thus might increase the overall radiative lifetime under a given temperature). The hole wavefunction in Fig.1(b) is localized on Se atoms, and forms a layer structure following the Se atoms. (2) When an external negative charge is placed near the Cd atom ($d=0.5\text{\AA}$), the hole wavefunction becomes spatially localized near that charge, although bulk like characteristic (layer structure on top of the Se atoms) still exists. Meanwhile, the electron wavefunction has been pushed away to the other side of the quantum dot. But the hole wavefunction is much more localized than the electron wavefunction. Partly, this is because the hole is closer to the external charge where the electric field is larger than the other side of the quantum dot. This could also be due to the fact that the hole has a larger effective mass than the electron. Notice that, the distance between the center-of-mass of the final localized hole state and the surface charge is about 3\AA according to z_{vbm} in Table.I. Calculated by a simple formula Z/d^2 , we have an unscreened electric field of $1.6 \times 10^8\text{ V/cm}$ at the final location of the hole. The unscreened electric field at the center of the quantum dot (which is the hole location before it has been pulled away by the electric field) is $3.8 \times 10^6\text{ V/cm}$. Both values are larger than the unscreened external electric field applied to the QD when Stark effects are studied for such systems (In Ref.[4], the maximum external electric field is $4 \times 10^5\text{ V/cm}$). Before the Coulomb interaction between electron and hole (V_{coul}) has been taken into account, the optical transition P has dropped to 0.006 of the uncharged result P_0 . After the Coulomb interaction, P recovers to 0.014 P_0 . This should cause significant quenching of the luminescence. Notice that, in this case, and all the charged quantum dot cases below, the electron-hole Coulomb interaction increases P by roughly a factor of 2. In the following, we will only discuss the final P values after the Coulomb interaction, which is related to the radiative life time. (3) When the negative charge moves away from the surface, the P

recovers quickly. For example, when $d = 1.5\text{\AA}$, the P is $0.14P_0$, ten times larger than the result of $d = 0.5\text{\AA}$. When $d = 2.5\text{\AA}$, P increases to $0.5P_0$, and when $d = 4.5\text{\AA}$, P is $0.7P_0$. Thus, in order for this trapped charge to significantly quench the luminescence, it must be located near the surface of the quantum dot, probably at the dangling bonds of the Cd atom (for the case of core CdSe dot). (4) Corresponding to the reduction of the optical transition P , the band gaps are also reduced from the uncharged case. The band gap (including the electron-hole Coulomb energy) reduction for $d=0.5, 1.5, 2.5, 4.5\text{\AA}$, are 173,67,36,21 meV respectively. The dependence to d is not as sensitive as the P . Notice that these band gap reductions are slightly larger than the energy spectral shiftings of a single QD [4, 7], which are usually within 20 meV. This implies that the spectral shifting is caused by charges located not at the QD surface, but about 5\AA away from the surface.

Besides the results in Table I, we have also performed other calculations to get a more complete picture of the effect of external charges on the PL. We summarize the results here:

(a) In order to see the effect of different charges, we have replaced the negative charge with a positive charge (a trapped hole), again 0.5\AA away from the top Cd atom. This time, the final P is reduced only by a factor of 1.5, not enough to cause a significant PL quenching.

(b) However, it is interesting to know the effect when a positive charge is placed near a Se atom, especially since a unpassivated Se atom is a hole trapping site [19]. To do this, we first exchanged the Cd and Se atoms in our quantum dot. We call the resulting $Se_{534}Cd_{527}$ quantum dot an inverse dot of the original $Cd_{534}Se_{527}$ dot. Notice that, we are doing a non-selfconsistent calculation for the single particle potential V_{dot} , our result is not sensitive to the stoichiometry of the system. This allows us to exchange the Cd and Se atoms (and their corresponding ligand passivations) without causing erroneous effects. The reason to exchange Se and Cd atom is to have a completely symmetric treatment between electron and hole, cation and anion. The band gap and the P of this inverse dot is almost the same as the original dot for the uncharged case. However, when a positive charge is placed 0.5\AA away from the top Se atom, we find an extra eigen state inside the band gap and located on top of the point charge. In an ab initio calculation where the trapped charge is represented by dangling bond wavefunctions, rather than a point, such hydrogen like state may or may not exist. If we ignore this hydrogen like state, then the final P between the CBM and VBM is $0.0013P_0$, 10 times smaller than the case in Table I. But the situation here is complicated by the existence of the extra band gap

state, more reliable ab initio calculations are needed here.

(c) To see the effects of the magnitude of the charge, we have repeated the calculation of the original quantum dot with a $-2e$ negative charge. This time, even when d is 4.5\AA , the final P is $0.0015 P_0$. Thus, it has a long range effect. For shorter distance d , the corresponding P is also significantly smaller than the values in Table I.

(d) To see whether the result depends sensitively on the direction, we have placed the $-e$ negative charge near a Cd atom at the equator of the quantum dot. Like the Cd atom on the top of the quantum dot, this Cd atom also has one dangling bond. Again, with a charge-Cd atom distance of 0.5\AA , we get $P = 0.2P_0$. Although this is enough to produce a significant quenching of the PL, P is 10 times larger than the case when the $-e$ is near a Cd atom on the top of the quantum dot. This indicates a strong directional dependence. This dependence can be partially explained by the layer structure of the hole wavefunction as shown in Fig.1(b). The hole wavefunction has a semi-node between the layers (Fig.1), which makes it easier to be truncated (thus localized) on the z direction.

(e) In all the above calculations, only one charge is used. However, if PL intermittency is caused by trapped charges, it is more likely that there are both a positive charge and a negative charge trapped near the surface, produced from a single electron-hole pair ionization. To investigate this possibility, we have placed a positive charge at the bottom of the quantum dot, 0.5\AA away from a Se layer, in addition to the negative charge 0.5\AA away from the Cd atom on the top of the quantum dot. The resulting P is 30 times smaller than the case of a single negative charge ($d = 0.5\text{\AA}$ in Table I). This is the strongest quenching charge configuration we have found in this study. We have also placed the additional positive charge at the equator, forming a 90° angle with the negative charge on the top of the quantum dot. This time, we found that the resulting P is a factor of 2 smaller than the single negative charge result. Thus, in both cases, the additional positive charge further reduces the P .

(f) Finally, we like to know the size dependence of the above effects. Here we have chosen one smaller size quantum dot: $Cd_{81}Se_{83}$ (which has a diameter of 21\AA), and studied only the effects of a negative charge near a Cd atom (with one dangling bond) on the top of the quantum dot. The final P for the uncharged dot is 0.107 (a.u), very close to the result of the $Cd_{534}Se_{527}$ dot. When the external negative charge is placed at $d=0.5, 1.5, 2.5, 4.5\text{\AA}$, the reduced final P 's (including the Coulomb interaction) are: $0.0064, 0.012, 0.026, 0.062$ (a.u), respectively. Comparing to Table I,

for $d=0.5\text{\AA}$, the small dot has a smaller P , but for larger distance d 's, the situation is reversed. The overall d dependence of P for this smaller dot is smaller than the larger dot. The reason behind this might be complicated. There are competitions between quantum confinement effects, atomistic layer structure, electric field and screening. They scale differently with the quantum dot size.

To summarize the above results, we conclude that: (1) When a negative trapped charge is on the surface near a top Cd atom, it is enough to pull the electron and hole apart to cause a significant reduction (70 folds) on the radiative decay rate. (2) This effect is largest when a negative charge is on the top of the QD, while a positive charge is at the bottom of the QD. Then the reduction of the radiative decay rate could be 2000 folds. (3) However, this quenching effect decays quickly when the charge is moved away from the surface. (4) There are also sensitive directional and local atomic environmental dependences of this quenching effect. (5) The PL energy change due to the existence of the external charge matches that in the spectral shifting experiment[4, 7] when the charge is about 5\AA away from the surface.

Given the calculated results summarized above, we can now discuss the plausibility of the trapped charge model for the PL intermittency. What the calculations have showed is that there are some charge trapping sites ("strong sites") where a trapped charge can reduce the radiative rate significantly (e.g., 2000 folds). However, there are also other charge trapping sites ("weak sites") (e.g., near the equator) which do not have such strong effects. So, if the trapped charge model is going to work, the picture will be the following. When an ionization happens to the "strong sites", we will see a "complete" PL quenching (off-period). But even for a same QD, there could be ionization happens to the "weak sites". In that case, the PL quenching is incomplete, and this might correspond to the experimentally observed different PL intensities during the on-period. In most experiments, the CdSe quantum dot is capped with a ZnS layer. In that case, in order for the trapped charge model to work, the trapped charge must be localized at the CdSe:ZnS interface. In that case, although the thin ZnS layer might provide a little additional screening (which reduces the pulling power of the trapped charge), it also provides additional space with low barrier heights for the electron and hole to be separated apart. Thus the net result might be similar to the core QD with a charge on its surface. Unfortunately, there are not enough experiments to judge how good is the epitaxial shell layer and how plausible it is for the charge to be trapped at the interface.

More reliable ab initio calculations and experiments are needed to prove or disprove different PL intermittency models.

Before ending this article, we like to make a few comments about our calculations. For simplicity, we have only reported the optical matrix elements between the VBM and CBM states, but at room temperature, higher states might become relevant. Due to the wurtzite structure, there is no degeneracy in the VBM and CBM. For the $Cd_{534}Se_{527}$ uncharged quantum dot, the next conduction band state (CBM+1) is 250meV above the CBM, while the next valence band state (VBM-1) is only 20meV below the VBM state. Thus, at room temperature, while the CBM+1 might not be important, the VBM-1 is. When a negative charge is near the quantum dot, the VBM-1/VBM energy splitting $\Delta E(VBM - 1/VBM)$ can be changed in both ways. When $\Delta E(VBM - 1/VBM)$ is large (60 meV, for the $d=0.5\text{\AA}$ case, where VBM is much more localized than VBM-1), the $P(VBM - 1/CBM)$ can be much (10 times) larger than $P(VBM/CBM)$. When $\Delta E(VBM - 1/VBM)$ is small (10 meV), the $P(VBM - 1/CBM)$ becomes similar (within a factor of 2) to $P(VBM/CBM)$. Thus, when the VBM-1 state is taken into account at the room temperature, the trends of $\Delta E(VBM - 1/VBM)$ and $P(VBM - 1/CBM)$ are mutually cancelling each other. As a result, our conclusions above might not be affected by the room temperature. We also did not consider the exchange splitting between the electron and hole state. But that splitting is about 5 meV in our quantum dot [15], thus should not change the situations either at room temperature.

The biggest approximation in our calculations is the use of point trapped charge and the continuum classical model for its dielectric screening. These prevent us from atomistic treatment of the local screening response near the surface. For the dielectric constant in Eqs(2) and (3), we have used $\epsilon = \epsilon_{ion} + \epsilon_{dot}$. Here the size dependent ϵ_{dot} is obtained from previous calculations[14] (5.57 for $Cd_{534}Se_{527}$, 4.90 for $Cd_{81}Se_{83}$). We have included $\epsilon_{ion} = 3.5$ for the ionic response. This could be an over estimation of the total ϵ . A reduction of ϵ is like an increase of the external charge. Its dramatic effect (to further reduce P) has been demonstrated in the -2e negative charge calculation in the above item (c).

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Table 1: The results for the $Cd_{534}Se_{527}$ quantum dot with one negative charge distance d away from a top surface Cd atom. E_g is the band gap. z_{vbm} and z_{cbm} are the center of mass positions of VBM and CBM wavefunction squares, with zero defined at one Se layer at the middle of the quantum dot. P is the VBM-CBM optical transition matrix-element-square. The top rows are for the results without the electron-hole Coulomb interactions, and the bottom rows are results with the Coulomb interactions.

$d(\text{\AA})$	uncharged	0.5	1.5	2.5	4.5
$E_g(\text{eV})$	2.296	2.065	2.183	2.229	2.257
$z_{vbm}(\text{\AA})$	-0.02	16.66	13.39	9.83	6.83
$z_{cbm}(\text{\AA})$	-0.75	-3.58	-3.41	-3.25	-2.96
P (a.u)	0.129	0.75E-3	0.99E-2	0.28E-1	0.55E-1
E_g (eV)	2.161	1.988	2.094	2.125	2.140
$z_{vbm}(\text{\AA})$	-0.25	16.44	12.45	7.38	4.66
$z_{cbm}(\text{\AA})$	-0.61	-2.45	-2.09	-1.82	-1.60
P (a.u)	0.127	0.18E-2	0.19E-1	0.61E-1	0.91E-1

Figure 1: The electron (a),(c), and hole (b),(d) wavefunctions squares for the $Cd_{534}Se_{527}$ quantum dot. A cross section of the quantum dot is shown. (a) and (b) are the results for uncharged dot, while (c) and (d) are under the influence of a negative point charge, as indicated by the arrow in (d). The circle in (d) denotes the surface of the quantum dot. All the results have included the electron-hole Coulomb interactions.